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Syntheses and Characterization of Gold(I) and Platinum(II) Complexes Containing Tris(2-cyanoethyl)phosphine. X-ray Crystal Structures of [(CEP)$_2$Au]Cl, *cis*-(CEP)(Et$_2$S)PtCl$_2$, and *trans*-(CEP)$_2$PtCl$_2$

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The following gold(I) and platinum(II) complexes of tris(2-cyanoethyl)phosphine, CEP, have been synthesized: (CEP)AuCl (**1**), [(CEP)$_2$Au]Cl (**2**), *cis*-(CEP)(Et$_2$S)PtCl$_2$ (**3**), *trans*-(CEP)$_2$PtCl$_2$ (**4**). The structures of **2**–**4** are reported here. Compound **2** crystallized in the trigonal (hexagonal) space group $R3c$ (No. 167) with unit cell $a = 12.216(2)$ Å, $c = 25.885(7)$ Å, $\gamma = 120°$, $V = 3345(1)$ Å^3, and $Z = 6$. The Au(I) center is encapsulated by six CN groups of two P(CH$_2$CH$_2$CN)$_3$ ligands. The cation structure has S_6 point group symmetry. Refinement of 780 reflections and 44 parameters yielded $R = 0.0256$ and $R_w = 0.0268$. The Au(I)–P distance is 2.314(2) Å, and the average nonbonding Au(I)···N distance for CN groups is 3.579(3) Å. Compound **3** crystallized in the monoclinic space group $P2_1/c$ (No. 14) with unit cell $a = 12.029(8)$ Å, $b = 7.432(5)$ Å, $c = 21.43(2)$, $\beta = 93.17(6)°$, $V = 1911(2)$ Å^3, and $Z = 4$. Refinement of 2888 reflections and 195 parameters yielded $R = 0.0474$ and $R_w = 0.0348$. The average Pt–Cl distance is 2.353(5) Å, the Pt–P distance is 2.250(5) Å, and the Pt–S distance is 2.298(5) Å. Compound **4** crystallized in the orthorhombic space group *Pcab* (No. 61) with unit cell $a = 14.14(1)$ Å, $b = 4.17(1)$ Å, $c = 18.87(2)$ Å, $V = 2445(4)$ Å^3, and $Z = 4$. Refinement of 1847 reflections and 133 parameters yielded $R = 0.0400$ and $R_w = 0.0384$. Both CEP ligands in [(CEP)$_2$Au]Cl encapsulate the gold(I) atom while in (CEP)$_2$PtCl$_2$ the ligands form an inverted "umbrella" relative to Pt(II). The Pt–Cl distance is 2.317(3) Å, and the Pt–P distance is 2.312(3) Å. Hydrolysis of **2** at 120 °C in the presence of H$_2$SO$_4$/H$_2$O gives ClAu[P(CH$_2$CH$_2$COOH)$_3$]$_2$.

Introduction

Tris(2-cyanoethyl)phosphine (CEP) was first synthesized by Rauhut et al.[1] in 1959. The phosphorus atom is reported to be a much poorer base[2] in CEP than in P(CH$_2$CH$_3$)$_3$. The CEP ligand forms strong metal–phosphorus bonds in metal complexes.[3-9] Complexes that have been characterized crystallographically are Ni$_4$(CO)$_6$[P(CH$_2$CH$_2$CN)$_3$]$_4$,[3] β-NiCl$_2$[P(CH$_2$CH$_2$CN)$_3$]$_2$,[4] Ni(NCS)$_2$[P(CH$_2$CH$_2$CN)$_3$]$_2$,[5] M(CO)$_5$P(CH$_2$CH$_2$CN)$_3$ (M = Mo, Cr),[2] [HgBr$_2${P(CH$_2$CH$_2$CN)$_3$}$_2$]·Me$_2$CO[6] and [HgCl$_2$P(CH$_2$CH$_2$CN)$_3$]$_n$.[6] Square-planar monomeric chloro and bromo Ni(II) complexes condense in the solid state to form octahedral polymers, where the nickel centers are coordinated to bridged –PCH$_2$CH$_2$C≡N– moieties.[7-9] A few Co(II) and Pt(II) complexes with this ligand have been reported,[7] but not characterized crystallographically. The compound (CEP)$_2$PtCl$_2$ was prepared[7] from a direct reaction between K$_2$PtCl$_4$ and P(CH$_2$CH$_2$CN)$_3$.

Two properties of CEP prompted us to examine the structures of Au(I) and Pt(II) CEP complexes. First, do the CN groups also participate in the coordination? With Au(I) does this coordination sterically block gold–gold interactions, producing isolated (mononuclear) low-coordinate gold(I) centers? 1,3-Dicyano propane is known[10] to bond to Rh(I) through the CN groups. Second, would the ligand hydrolyze and remain coordinated to the metal? While we were reasonably certain that phosphine coordination would occur, the orientation of the terminal CN groups and their potential for bonding were uncertain.

We report here the syntheses of (CEP)AuCl (**1**), (CEP)$_2$AuCl (**2**), *cis*-(CEP)(Et$_2$S)PtCl$_2$ (**3**), and *trans*-(CEP)$_2$PtCl$_2$ (**4**), X-ray structural studies of **2**–**4**, and the hydrolysis of [(CEP)$_2$Au]Cl.

Experimental Section

The ligand P(CH$_2$CH$_2$CN)$_3$, 95% pure, was purchased from Strem Chemical Inc. and used without further purification. The compounds *cis*-(Et$_2$S)$_2$PtCl$_2$ and (THT)AuCl (THT = tetrahydrothiophene) were synthesized by following the literature procedures.[11,12] Solvents were rigorously dried over appropriate drying agents and distilled under N$_2$ prior to use. All reactions were carried out in an atmosphere of prepurified dinitrogen. IR spectra were recorded on a Perkin-Elmer 783 infrared spectrophotometer, and ^{31}P{^{1}H} NMR spectra were recorded on Varian XL-200 and XL-400 spectrometers using an internal deuterium lock and 85% H$_3$PO$_4$ as an external standard.

Synthesis of [Tris(2-cyanoethyl)phosphine]gold(I) Chloride, (CEP)AuCl (1). To a stirred solution of (THT)AuCl (100 mg, 0.31 mmol) in 5 mL of CH$_2$Cl$_2$/CH$_3$CN (3:2 by volume) was added CEP (60.2 mg, 0.31 mmol) in one portion to yield a clear, colorless solution. The resultant mixture was stirred for 1 h at room temperature. Upon addition of diethyl ether (3 mL), a white solid was isolated in a 95% yield (126 mg). The white solid was recrystallized from CH$_2$Cl$_2$/Et$_2$O (1:1, 6 mL) mixture. IR (NaCl, Nujol mull): ν(CN) 2240 (s) cm^{-1}. ^{31}P{^{1}H} NMR in CDCl$_3$/CH$_3$CN (1:1): δ 27.28 (s). Two crystallographic forms of the molecule have been observed and will be reported elsewhere.

Synthesis of Bis[tris(2-cyanoethyl)phosphine]gold(I) Chloride, [(CEP)$_2$Au]Cl (2). (THT)AuCl (305.3 mg, 0.95 mmol) was dissolved in 10 mL of CH$_2$Cl$_2$/CH$_3$CN (1:1 by volume). To this while being

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stirred was added CEP (367.60 mg, 1.90 mmol) in one portion to give a colorless clear solution. The mixture was stirred for 2 h. A white solid was precipitated with Et_2O and recrystallized from a mixture of CH_3CN/Et_2O by either slow diffusion of Et_2O into a CH_3CN solution or dissolution of the solid in a mixture of CH_3CN/Et_2O (5 mL/2 mL) and storing it in a refrigerator overnight to yield (530 mg, 90%) a colorless crystalline product. IR: ν(CN) 2240 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR in $CDCl_3/CH_3CN$ (2:1): δ 32.51 (s). The same compound was also readily obtained by treatment of (CEP)AuCl with 1 equiv of CEP.

Synthesis of *cis*-[Tris(2-cyanoethyl)phosphine](diethyl sulfide)platinum(II) Dichloride, (CEP)(Et_2S)$PtCl_2$ (3). [$(CEP)_2Au$]Cl (30 mg, 0.048 mmol) was added to a stirred yellow solution of $(Et_2S)_2PtCl_2$ (21.6 mg, 0.048 mmol) in CH_2Cl_2 (3 mL). The resultant light yellow solution was stirred overnight. Then Et_2O was added to the now colorless CH_2Cl_2 solution to yield a white solid. The solid was further dissolved in CH_3CN to separate *cis*-(CEP)(Et_2S)$PtCl_2$ from (CEP)AuCl (insoluble in CH_3CN). Upon addition of Et_2O to the CH_3CN solution, pale yellow crystals of *cis*-(CEP)(Et_2S)$PtCl_2$ were formed in a 90% yield. IR (NaCl, Nujol mull): ν(CN) 2245 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR in $CDCl_3/CH_3CN$ (2:1): δ 11.43 (s), $J(^{195}Pt-P)$ = 2500 Hz.

Synthesis of *trans*-Bis[tris(2-cyanoethyl)phosphine]platinum(II) Dichloride, $(CEP)_2PtCl_2$ (4). To a stirred solution of $(Et_2S)_2PtCl_2$ (20 mg, 0.044 mmol) in CH_2Cl_2 (3 mL) was added CEP (17.3 mg, 0.088 mmol) in one portion. A light yellow solid immediately precipitated; it dissolved upon addition of CH_3CN (4 mL), giving a yellow solution. This solution was further stirred for 3 h at room temperature. Upon addition of Et_2O (2 mL) to the yellow solution, a light yellow solid (microcrystalline) slowly precipitated (21.9 mg) in a 75% yield over 3 h at room temperature. IR (NaCl, Nujol mull): ν(CN) 2240 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR in $CDCl_3/CH_3CN$ (2:1): δ 10.86 (s), $J(^{195}Pt-P)$ = 2518 Hz.

Hydrolysis of –CN to –COOH and NH_3. To a stirred solution of [$(CEP)_2Au$]Cl (2) (300 mg, 0.49 mmol) in H_2O (1 mL) was added dropwise H_2SO_4 (1 mL) at room temperature. The resulting solution was heated at 120 °C overnight. H_2O was removed by distillation, leaving a viscous liquid. Upon addition of 2-propanol (5 mL) to the viscous liquid, a colorless solid, [$\{P(CH_2CH_2COOH)_3\}_2Au$]Cl (5), was precipitated. The colorless solid (100 mg, 30%) was isolated by filtration. IR (Nujol mull): ν(CO) 1730 (b) cm^{-1}. $^{31}P\{^1H\}$ NMR in D_2O: δ 42.86 (s). Compound **5** is very hygroscopic. Mp: 250–252 °C to a purple solution. Anal. Calc (found) for $C_{18}H_{30}O_{12}P_2ClAu\cdot 3H_2O$: C, 27.47 (27.50); H, 4.61 (4.60); Au, 25.03 (24.95).

X-ray Structure Determination. Compounds **2–4** were recrystallized from CH_3CN, $CH_3CN/CHCl_3$, and CH_3CN/CH_2Cl_2, respectively, by slow diffusion of Et_2O. Crystals were mounted on glass fibers with epoxy resin. The diffractometer (Nicolet R3m/E diffractometer; SHELXTL 5.1) and procedures used have been previously described.[13]

Unit cell constants were determined from 25 machine-centered reflections. Data were collected using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 293 K. The crystals showed no significant decay during data collection. All data were corrected for Lorentz and polarization effects and for absorption by empirical methods based on azimuthal data.

All structures were solved by standard Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions (C–H = 0.96 Å; $U(H) = 1.2U_{eq}(C)$). Crystallographic data are recorded in Table I. Atomic positional and thermal parameters for **2–4** are given in Tables II, IV, and VI; bond lengths and angles are recorded in Tables III, V, and VII.

Results

Addition of 1 and 2 equiv of CEP to (THT)AuCl gives (CEP)AuCl (**1**) and [$(CEP)_2Au$]Cl (**2**), respectively. The structure of **2** (Figure 1) places Au, P, and Cl on a 3-fold rotational axis with Au at the inversion center; Cl is on a position with 32 symmetry midway between two cations. The cation has S_6 symmetry. *The gold atom is encapsulated by six –CN groups with an Au···N separation of 3.579(3) Å.*

The position of the ν(CN) band in the IR spectrum of **1** and **2** is the same as in the free ligand, 2240 cm^{-1}, indicating that there is no important metal–CN interaction. The CAChe modeling package (Computer Aided Chemistry; CAChe Scientific Inc., Beaverton, OR) was used to explore the MM2 structure of the complex. The first geometry obtained using known connectivities, a linear P–Au–P geometry, and the normal MM2 parameters was the inverted umbrella geometry as observed for the trans Pt(II) complex, $(CEP)_2PtCl_2$ (Figure 3). A scan of energy minima obtained by allowing only single-bond rotations showed that the encapsulated double-umbrella geometry was another minimum on the energy surface.

Compound **2** is soluble in water at room temperature. In an attempt to hydrolyze –CN to –COOH and NH_3, **1** and **2** were each treated with H_2SO_4/H_2O at 120 °C. The reactions shown in Scheme I were observed. The Au(I) center in (CEP)AuCl decomposes in H_2SO_4/H_2O at 120 °C to metallic gold. In contrast, no sign of decomposition or reduction of the Au(I) center to metallic gold was observed on overnight heating of [$(CEP)_2Au$]Cl in H_2SO_4/H_2O. Hydrolysis of the –CN group occurred instead, giving [$\{P(CH_2CH_2COOH)_3\}_2Au$]Cl. The IR spectrum of this hydrolysis product has a peak at 1730 (b) cm^{-1} that is attributed to the carbonyl in –COOH. No peak was observed around 2240 cm^{-1} for residual CN groups. The $^{31}P\{^1H\}$ NMR spectrum contains a single peak at 42.86 ppm which is significantly shifted from the peak observed for **2**, 32.51 ppm.

Addition of CEP to *cis*-$(Et_2S)_2PtCl_2$ in a 1:1 ratio gives *cis*-(CEP)(Et_2S)$PtCl_2$ (**3**) after 3 h at room temperature. No Pt···CN

Table I. Crystallographic Data for Compounds **2–4**

	2	**3**	**4**
formula	$C_{18}H_{24}N_6P_2ClAu$	$C_{13}H_{22}N_3SPCl_2Pt$	$C_{18}H_{24}N_6P_2Cl_2Pt$
fw	618.795	549.37	664.47
crystal system	trigonal	monoclinic	orthorhombic
space group	*R*3*c* (No. 167)	$P2_1/c$ (No. 14)	*Pcab* (No. 61)
a, Å	12.216(2)	12.029(8)	14.14(1)
b, Å	12.216(2)	7.432(5)	4.17(1)
c, Å	25.885(7)	21.43(2)	18.87(2)
α, deg	90	90	90
β, deg	90	93.71(6)	90
γ, deg	120	90	90
V, Å^3	3345(1)	1911(2)	2445(4)
Z	6	4	4
d_{calc}, g/cm^3	1.843	1.909	1.80
μ(Mo Kα), cm^{-1}	68.6	81.82	63.96
transm factors: max, min	0.959, 0.585	0.950, 0.569	0.938, 0.699
R,[a] R_w[b]	0.256, 0.268	0.0474, 0.0348	0.0400, 0.0384

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)[a] for [$((NCCH_2CH_2)_3P)_2Au$][Cl] (**2**)

atom	*x*	*y*	*z*	U_{iso}[b]
Au	0	0	0	25(1)
P	0	0	894(1)	24(1)
C(1)	1494(5)	1178(6)	1185(2)	33(3)
C(2)	2677(5)	1287(5)	923(2)	35(3)
C(3)	2975(5)	1971(6)	424(2)	34(3)
N	3219(4)	2505(5)	49(2)	51(3)
Cl	0	0	2500	96(3)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] The equivalent isotropic *U* defined as one-third of the trace of the U_{ij} tensor.

Table III. Bond Lengths (Å) and Angles (deg)[a] for [$((NCCH_2CH_2)_3P)_2Au$][Cl] (**2**)

Au–P	2.314(2)	P–C(1)	1.828(5)
C(1)–C(2)	1.540(9)	C(2)–C(3)	1.482(8)
C(3)–N	1.123(8)		
Au–P–C(1)	114.3(2)	C(1)–P–C(1′)	104.2(2)
P–C(1)–C(2)	114.3(4)	C(1)–C(2)–C(3)	112.8(6)
C(2)–C(3)–N	178.9(6)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

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Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)^a for $[P(CH_2CH_2CN)_3][S(CH_2CH_3)]PtCl_2$ (**3**)

atom	*x*	*y*	*z*	U_{iso}^{b}
Pt	3266(1)	5499(1)	6543(1)	42(1)*
Cl(1)	4410(4)	6812(7)	5827(2)	66(2)*
Cl(2)	3705(4)	7956(7)	7218(2)	66(2)*
S	2190(4)	4119(7)	7251(2)	53(2)*
C(41)	1550(13)	5739(26)	7778(7)	74(8)*
C(42)	719(4)	6827(32)	7389(9)	105(12)*
C(51)	3196(12)	2935(26)	7781(8)	68(8)*
C(52)	2626(16)	1714(29)	8238(9)	93(11)*
P	2931(4)	3270(7)	5845(2)	48(2)*
C(11)	4208(12)	2185(25)	5615(7)	58(8)*
C(12)	5014(13)	1683(26)	6137(8)	82(9)*
C(13)	6068(13)	948(23)	5890(7)	61(8)*
N(1)	6825(11)	412(25)	5690(6)	87(7)*
C(21)	2299(20)	3969(26)	5071(10)	111(11)
C(22a)	2440(31)	5342(61)	4782(18)	72(14)
C(22b)	1432(25)	5123(42)	5106(14)	59(12)
C(23a)	1535(38)	6045(63)	4337(23)	49(15)
C(23b)	1010(43)	5893(72)	4473(23)	91(18)
N(2)	785(15)	6493(24)	3992(9)	103(9)*
C(31)	2005(13)	1501(20)	6069(8)	63(8)*
C(32)	1812(13)	17(22)	5611(9)	87(10)*
C(33)	712(17)	−963(27)	5707(10)	73(10)*
N(3)	−97(16)	−1706(27)	5802(10)	118(11)*

^{a} Estimated standard deviations in the least significant digits are given in parentheses. ^{b} For values with asterisks, the equivalent isotropic *U* is defined as one-third of the trace of the U_{ij} tensor.

Table V. Bond Lengths (Å) and Angles (deg)^a for $[P(CH_2CH_2CN)_3][S(CH_2CH_3)_2]PtCl_2$ (**3**)

Pt–Cl(1)	2.340(5)	Pt–Cl(2)	2.367(5)
Pt–S	2.298(5)	Pt–P	2.250(5)
S–C(41)	1.852(18)	S–C(51)	1.831(17)
C(41)–C(42)	1.503(26)	C(51)–C(52)	1.530(27)
P–C(11)	1.831(16)	P–C(21)	1.854(21)
P–C(31)	1.807(16)	C(11)–C(12)	1.479(22)
C(12)–C(13)	1.507(24)	C(13)–N(1)	1.105(22)
C(21)–C(22a)	1.210(48)	C(21)–C(22b)	1.357(38)
C(22a)–C(23a)	1.495(60)	C(22b)–C(23b)	1.528(58)
C(23a)–N(2)	1.177(49)	C(23b)–N(2)	1.140(53)
C(31)–C(32)	1.485(24)	C(32)–C(33)	1.537(27)
C(33)–N(3)	1.148(29)		
Cl(1)–Pt–Cl(2)	87.8(2)	Cl(1)–Pt–S	177.8(2)
Cl(2)–Pt–S	93.1(2)	Cl(1)–Pt–P]	87.6(2)
Cl(2)–Pt–P	175.4(2)	S–Pt–P	91.5(2)
Pt–S–C(41)	112.7(6)	Pt–S–C(51)	104.2(6)
C(41)–S–C(51)	102.6(8)	S–C(41)–C(42)	107.1(12)
S–C(51)–C(52)	112.1(11)	Pt–P–C(11)	112.7(6)
Pt–P–C(21)	115.7(7)	C(11)–P–C(21)	100.7(9)
Pt–P–C(31)	116.5(6)	C(11)–P–C(31)	107.0(8)
C(21)–P–C(31)	102.6(9)	P–C(11)–C(12)	115.4(12)
C(11)–C(12)–C(13)	110.6(14)	C(12)–C(13)–N(1)	177.7(17)
P–C(21)–C(22a)	129.1(23)	P–C(21)–C(22b)	113.5(18)
C(22a)–C(21)–C(22b)	68.3(25)	C(21)–C(22a)–C(23a)	120.0(35)
C(21)–C(22b)–C(23b)	113.5(30)	C(22a)–C(23a)–N(2)	175.6(38)
C(22b)–C(23b)–N(2)	174.3(52)	C(23a)–N(2)–C(23b)	36.3(37)
P–C(31)–C(32)	115.9(13)	C(31)–C(32)–C(33)	111.3(15)
C(32)–C(33)–N(3)	177.4(22)		

^{a} Estimated standard deviations in the least significant digits are given in parentheses.

Table VI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)^a for $(P(CH_2CH_2CN)_3)_2PtCl_2$ (**4**)

atom	*x*	*y*	*z*	U_{iso}^{b}
Pt	0	0	0	23(1)
P	610(2)	217(3)	−1132(2)	23(1)
Cl	−1129(2)	1724(4)	−302(2)	43(1)
C(11)	−45(7)	−845(14)	−1793(6)	36(4)
C(12)	−1121(8)	−712(13)	−1752(6)	36(4)
C(13)	−1598(7)	−1616(13)	−2292(7)	34(4)
N(1)	−1932(8)	−2313(11)	−2721(5)	51(4)
C(21)	1802(7)	−526(12)	−1276(6)	27(4)
C(22)	2561(7)	289(12)	−845(6)	37(4)
C(23)	3501(9)	−511(14)	−890(8)	54(5)
N(2)	4181(7)	−1093(15)	−932(9)	103(7)
C(31)	625(8)	2080(10)	−1514(5)	29(4)
C(32)	999(9)	3244(12)	−970(6)	44(5)
C(33)	1212(10)	4612(14)	−1347(7)	49(5)
N(3)	1386(10)	5648(13)	−1671(7)	75(6)

^{a} Estimated standard deviations in the least significant digits are given in parentheses. ^{b} The equivalent isotropic *U* defined as one-third of the trace of the U_{ij} tensor.

Table VII. Bond Lengths (Å) and Angles (deg)^a for $(P(CH_2CH_2CN)_3)_2PtCl_2$ (**4**)

Pt–P	2.312(3)	Pt–Cl	2.317(3)
Pt–P′	2.312(3)	Pt–Cl′	2.317(3)
P–C(11)	1.833(12)	P–C(21)	1.838(10)
P–C(31)	1.854(10)	C(11)–C(12)	1.528(15)
C(12)–C(13)	1.476(17)	C(13)–N(1)	1.135(16)
C(21)–C(22)	1.539(15)	C(22)–C(23)	1.520(17)
C(23)–N(2)	1.103(17)	C(31)–C(32)	1.572(16)
C(32)–C(33)	1.473(17)	C(33)–N(3)	1.157(18)
P–Pt–Cl	88.3(1)	Cl–Pt–P′	91.7(1)
P–Pt–Cl′	91.6(1)	P′–Pt–Cl′	88.4(1)
Pt–P–C(11)	113.2(4)	Pt–P–C(21)	116.5(4)
C(11)–P–C(21)	99.6(5)	Pt–P–C(31)	116.3(3)
C(11)–P–C(31)	103.4(5)	C(21)–P–C(31)	105.9(5)
P–C(11)–C(12)	115.2(8)	C(11)–C(12)–C(13)	112.0(10)
C(12)–C(13)–N(1)	177.3(12)	P–C(21)–C(22)	112.4(7)
C(21)–C(22)–C(23)	110.3(9)	C(22)–C(23)–N(2)	179.0(13)
P–C(31)–C(32)	112.1(7)	C(31)–C(32)–C(33)	109.4(10)
C(32)–C(33)–N(3)	176.8(14)		

^{a} Estimated standard deviations in the least significant digits are given in parentheses.

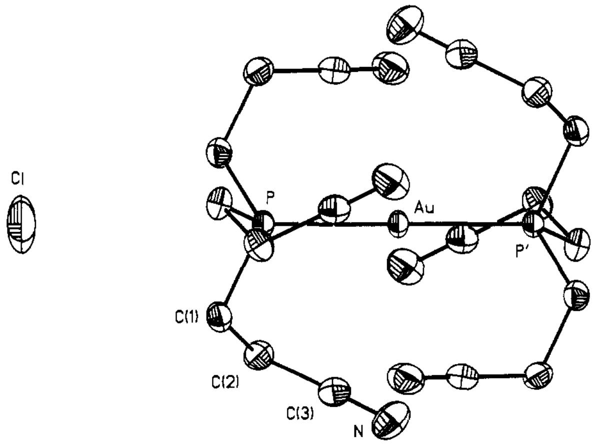


Figure 1. Structure of $[Au\{P(CH_2CH_2CN)_3\}_2]Cl$ (**2**) (40% ellipsoids viewed perpendicular to 3-fold axis).

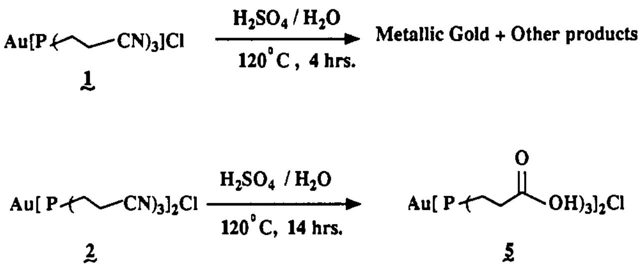
interaction is observed in the crystal structure (Figure 2). The IR spectrum also shows no CN perturbation. $^{31}P\{^1H\}$ NMR spectrum shows only one compound in solution. An indirect route to **3** also was found. *cis*-$(Et_2S)_2PtCl_2$ and $[(CEP)_2Au]Cl$ were mixed in a 1:1 ratio. The products obtained after crystallization from CH_3CN were **3** and (CEP)AuCl.

Addition of CEP to **3** in a 1:1 ratio immediately gives *trans*-$(CEP)_2PtCl_2$ (**4**). $^{31}P\{^1H\}$ NMR shows only one compound in solution; the Pt–P coupling constant, 2518 Hz, is consistent with trans geometry for a bis(phosphine)platinum(II) dihalide. Complex **4** shows the CEP ligands to have inverted umbrella conformations (Figure 3). The platinum atom is on a crystallographically imposed inversion center. In the presence of Et_2S, **3** slowly disproportionates to **4** and $(Et_2S)_2PtCl_2$.

Discussion

There is no evidence of metal···CN interactions between gold(I) or platinum(II) and coordinated CEP. The CN stretches at 2245 cm^{-1} for **3** and at 2240 cm^{-1} for **1**, **2**, and **4** are nearly the

Scheme I



same as that for the free ligand, 2240 cm^{-1}. This is consistent with the crystal structures, which display nonbonding distances between the –CN groups and the metal atoms. Unlike $(Ph_3P)_2$-AuCl, which is three-coordinate with a P–Au–P angle of 132°,[14] the chloride in **2** is not coordinated to the gold. Compound **2** also is not luminescent as a solid, unlike[15] $Au(PPh_3)_2Cl$. The only other two-coordinate bis(phosphine)gold(I) chloride that has been crystallographically characterized is $[(P(cyclohexyl)_3)_2Au]Cl$.[16]

The encapsulation of the metal observed in **2** has not been described before in other metal CEP complexes. Although structurally suggestive of a gold···CN interaction, the Au···N separation, 3.58 Å, is considerably longer than the sum of van der Waals radii, 3.25 Å. According to the MM2 results of CAChe molecular modeling, the occurrence of the encapsulating conformation is to be expected in linearly coordinated P–M–P complexes since this conformation has practically the same energy as calculated for the inverted umbrella conformation. The chloride atoms coordinated to Pt(II) in *trans*-$(CEP)_2PtCl_2$ apparently prevent this conformation from being viable for this complex. The encapsulation of Au(I) gives rise to a strictly two-coordinate, linear P–Au–P geometry for **2** in the solid state, hence eliminating the luminescence generally observed[15] in three-coordinate species such as AuL_2X or $[AuL_3]X$.

The compounds $(Et_2S)_2PtCl_2$ (cis and trans) have been widely used as starting materials for the preparation of many platinum(II) phosphines and organometallic derivatives since the Et_2S is easily replaceable. A few compounds similar to **2** which contain both alkyl sulfide and phosphine ligands have been structurally characterized: *cis*-$[(Bz_2PMe)(Et_2S)PtCl_2$,[17] $[PPh_3(Bz_2S)PtCl_2]$ and $[(PPh_3)(S(Bz)Et)PtCl_2]$,[18] $[Bu_4N]_2[Pt_2(P_2O_5H_2)_4(SEt_2)_2]$.[19] As expected, the trans influence of the Et_2S ligand is smaller than that of CEP: the Cl–Pt bond trans to CEP, 2.367(5) Å, is longer than the Cl–Pt bond trans to Et_2S, 2.340(5) Å. Aside from the fact that no bonding interactions occur between the Pt(II) atoms and the CN groups, the structures of **3** and **4** are unremarkable.

Gold(I) phosphine complexes are widely used as antiarthritic and antitumor drugs.[20–22] Complexes such as Et_3PAuCl show some activity when administered orally.[23] Since CEP is less basic[24] than Et_3P and therefore somewhat less prone to be oxidized to the phosphine oxide, we were interested in learning whether or not the gold CEP complexes would hydrolyze into water-soluble carboxylate derivatives. Although (CEP)AuCl is destroyed by mineral acids, the $[(CEP)_2Au]Cl$ complex readily is hydrolyzed to $[\{P(CH_2CH_2COOH)_3\}_2Au]Cl$. This product, which could not be crystallized, is very soluble in water. Perhaps compounds such as (CEP)Au(thiol) or $(NCCH_2)_3PAu$(thiol) will find some utility as drugs. The hydrolytic solubility of the CEP ligand also suggests potential utility in the aqueous photochemistry of gold(I) phosphine complexes.

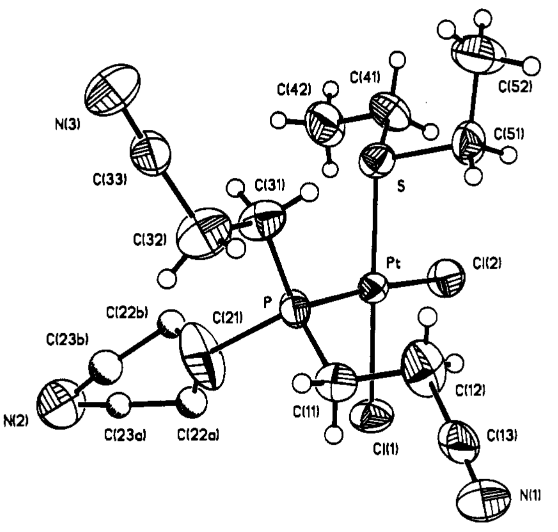


Figure 2. Structure of *cis*-$PtCl_2\{P(CH_2CH_2CN)_3\}(SEt_2)$ (**3**). Thermal ellipsoids have been drawn at the 40% probability level.

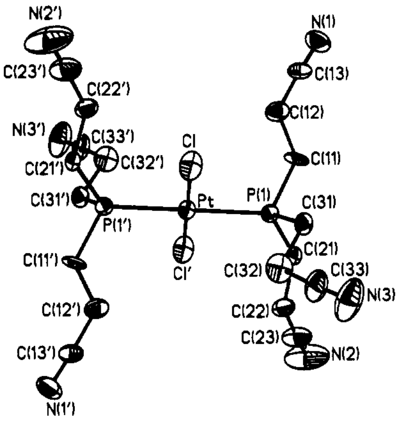


Figure 3. Structure of *trans*-$PtCl_2\{P(CH_2CH_2CN)_3\}_2$ (**4**). Thermal ellipsoids have been drawn at the 50% probability level.

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Supplementary Material Available: Tables of crystallographic data and experimental details, thermal parameters, and hydrogen coordinates (12 pages). Ordering information is given on any current masthead page.

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